

Spectroscopy of Electronic Defect States in Cu(In,Ga)(S,Se)_2 -based Heterojunctions and Schottky Diodes under Damp Heat Exposure

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The changes of defect characteristics induced by accelerated lifetime tests on the heterostructure $\text{n-ZnO/i-ZnO/CdS/Cu(In,Ga)(S,Se)}_2/\text{Mo}$ relevant for photovoltaic energy conversion are investigated. We subject heterojunction and Schottky devices to extended damp heat exposure at 85°C ambient temperature and 85% relative humidity for various time periods. In order to understand the origin of the pronounced changes of the devices, we apply current–voltage and capacitance–voltage measurements, admittance spectroscopy, and deep-level transient spectroscopy. The fill factor and open-circuit voltage of test devices are reduced after prolonged damp heat treatment, leading to a reduced energy conversion efficiency. We observe the presence of defect states in the vicinity of the CdS/chalcopyrite interface. Their activation energy increases due to damp heat exposure, indicating a reduced band bending at the Cu(In,Ga)(S,Se)_2 surface. The Fermi-level pinning at the buffer/chalcopyrite interface, maintaining a high band bending in as-grown cells, is lifted due to the damp-heat exposure. We also observe changes in the bulk defect spectra due to the damp-heat treatment.

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Cu(In,Ga)(S,Se)_2 -based thin film solar cells display relatively high energy conversion efficiencies on laboratory scale devices¹ as well as large area modules^{2,3}. These heterostructures basically consist of a transparent front contact (highly doped ZnO), a buffer layer (usually CdS), the Cu(In,Ga)(S,Se)_2 chalcopyrite absorber itself, and a back contact (e.g., Mo). An important key prerequisite for the success of this type of solar cells as a powerful source of renewable energy is their long-term stability under outdoor conditions. Encapsulated Cu(In,Ga)(S,Se)_2 based thin-film modules have been demonstrated to perpetuate their performance over many years under various environmental conditions, including the well-established damp heat (DH) test⁴. Non-encapsulated Cu(In,Ga)(S,Se)_2 -based solar cells, however, show losses in the fill factor and open-circuit voltage after DH exposure, whereas the short-circuit current remains almost unaffected. In the present study, we analyze the influence of accelerated lifetime tests on non-encapsulated $\text{ZnO/CdS/Cu(In,Ga)(S,Se)}_2/\text{Mo}$ heterostructure solar cells and $\text{Cr/Cu(In,Ga)(S,Se)}_2/\text{Mo}$ Schottky contacts, focussing on the electronic properties of the Cu(In,Ga)(S,Se)_2 absorber and the interface between window and absorber layer.

The samples investigated consist of non-encapsulated $\text{ZnO/CdS/Cu(In,Ga)(S,Se)}_2/\text{Mo}$ heterojunction solar cells and $\text{Cr/Cu(In,Ga)(S,Se)}_2$ Schottky contacts. The chalcopyrite absorber films (thickness about $1.5\mu\text{m}$) was fabricated via a two-step process based on rapid thermal processing of stacked elemental layers. A 20nm thick buffer layer of CdS was deposited on top of the Cu(In,Ga)(S,Se)_2 film in a chemical bath. The transparent front contact, a ZnO layer of about 800nm thickness, is deposited by r.f. and d.c. sputtering. The Schottky devices were processed by deposition of 50nm thick Cr film on top of the Cu(In,Ga)(S,Se)_2 film, followed by a 200nm

thick Au layer. Accelerated lifetime testing was performed under the standardized DH conditions at 85°C ambient temperature and 85% relative humidity for various time periods (24h, 144h, 294h, and 438h). The Schottky devices were exposed to the DH test only for 24h (before Cr/Au evaporation), as the effect of heat and humidity takes place on shorter time scales due to the lack of a protecting ZnO window layer. We have characterized the modification of the solar cell parameters of our samples using current–voltage measurements under AM 1.5 (solar spectrum) illumination at 25°C . Capacitance–voltage and admittance spectroscopy were performed using a Solartron 1260 impedance analyzer, deep-level transient spectroscopy (DLTS) by either applying a Semitrap 82E spectrometer or a custom-built transient DLTS setup based on a Boonton 7200 capacitance meter (response time about $120\mu\text{s}$). The Solartron impedance analyzer was operated with an alternating voltage of 30mV amplitude at frequencies in the range between 1Hz and 1MHz. The Semitrap spectrometer applies a fixed alternating voltage amplitude of 100mV, for the transient-DLTS setup we chose 50mV. In both cases, the sampling frequency for measuring the transients of the sample capacitance is 1MHz. The DLTS experiments typically included measurements with and without minority-carrier injection. In order to achieve the latter, filling pulses of 1.5V height and $100\mu\text{s}$ length superimposed on a quiescent reverse bias of -1.5V were applied. For minority-carrier injection, 0.5V forward bias pulses (superimposed on zero bias) were used. The transients were evaluated with exponential fits or the Laplace transform method⁵. Temperature-dependent analysis was performed using a helium closed-cycle cryostat. For this study, we have characterized about 50 samples. Most of the devices originated from the same process run, otherwise reference samples have been used to ensure comparability.

The effect of exposing our non-encapsulated test samples to water vapor manifests in losses in the fill factor and the open-circuit voltage (see fig. 1(a)). A slight kink in the current–voltage characteristics of the stressed devices can indicate an additional barrier being developed due to the DH exposure.

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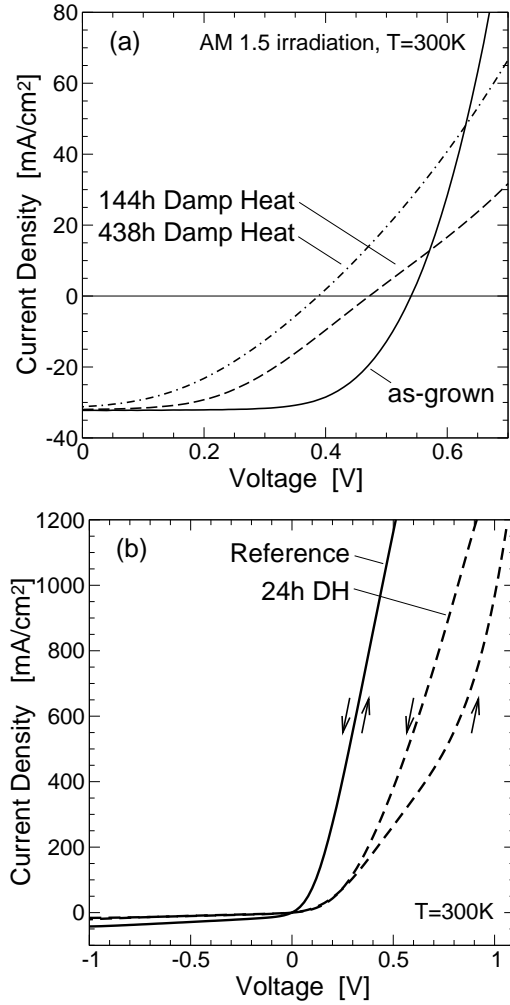


FIG. 1: Current-voltage characteristics of (a) Cu(In,Ga)(S,Se)₂-based heterojunction solar cells under AM 1.5 illumination and (b) Cr/Cu(In,Ga)(S,Se)₂ Schottky contacts. The hysteresis is also observed in DH treated solar cells.

However, we were not able to clearly show the existence of a second space charge region using admittance spectroscopy. A hysteresis of the current-voltage characteristics at forward bias can only be observed for the DH treated devices when the direction of the voltage sweep is changed. This effect is also seen in the DH treated Schottky contacts, as shown in fig. 1(b).

The effective doping density of the Cu(In,Ga)(S,Se)₂ based heterostructure samples was determined using capacitance-voltage (C - V) measurements. These experiments were performed at 90K temperature and 100kHz modulation frequency, in order to minimize the influence of deep levels. The slope of the resulting Mott-Schottky plots ($1/C^2$ versus V) clearly shows that the net doping concentration diminishes from $6 \times 10^{15} \text{cm}^{-3}$ for as-grown cells to about $2 \times 10^{15} \text{cm}^{-3}$ for cells after 144h and 438h of DH treatment. However, the built-in potential determined by this method is generally overestimated by approximately a factor of three.

A defect state at the CdS/Cu(In,Ga)(S,Se)₂ interface, fur-

ther on called β , can be observed using admittance spectroscopy or DLTS in heterostructure cells⁶ and Schottky contacts⁷. The properties of β determined by capacitance spectroscopy show that it is a defect state at the surface of the absorber layer (facing the buffer layer)^{6,7}. Thus, its activation energy represents the position of the Fermi level at the buffer/absorber interface relative to the conduction band⁶. A more detailed discussion of the facts indicating that β is located at the buffer/absorber interface is given in⁷. Cells exposed to the DH environment show a continuous shift of the activation energy and capture cross-section of the interface state β proportional to the exposure time. The main part of this shift proves to be irreversible. β is probably related to (S,Se) vacancies (dangling bonds) at this interface, which could also explain its sensitivity to oxygen⁸. As-grown Cu(In,Ga)(S,Se)₂-based solar cells usually show Fermi-level pinning at the buffer/absorber interface^{6,9}. The influence of DH treatment on devices that are exposed to the test conditions with the complete heterostructure gives rise to an unpinning of the Fermi level, which manifests in a shift of the interface state β when applying an external bias voltage. Devices containing DH treated absorbers, however, still show Fermi-level pinning.

A deep defect state, referred to as ϵ , is observed in DLTS spectra recorded before and after DH exposure. It is located in the absorber bulk. We observe minority and majority DLTS signals (depending on the amount of injected minority carriers during the filling pulse), both of them resulting in activation energies of about 550meV. Consequently, we expect the defect state ϵ to be a recombination center. Its capacitance transient at 350K for the case without injection pulses can be observed in fig. 2(a) for as-grown samples and in fig. 2(b) for cells exposed to DH conditions for 144h. The normalized amplitude $\Delta C/C_0$ of the capacitance transient related to ϵ is diminished due to the DH treatment. The origin of the deep defect state ϵ is currently unknown.

We observe a bulk acceptor-like defect state, γ , with DLTS in as-grown samples only. The corresponding capacitance transient at $T = 125\text{K}$ is shown in fig. 2(a). We determine an activation energy of about 160meV. Similar to ϵ , the normalized amplitude $\Delta C/C_0$ is diminished due to the DH treatment. Relating the determined defect activation energy to the calculations by Zhang et al.¹⁰, the defect state γ could possibly be an In vacancy.

A deep acceptor state, called ζ , is detected with admittance spectroscopy and DLTS in as-grown and DH treated Schottky contacts as well as in samples containing absorbers exposed to DH conditions. In samples DH treated as complete heterostructure, we observe ζ with DLTS with a relatively small amplitude, nevertheless manifesting an increase of its concentration relative to as-grown samples. The defect state corresponds to the fast decay of the capacitance transient of the DH treated sample at $T = 200\text{K}$, as shown in fig. 2(b). From the admittance data, we obtain an activation energy of about 380meV for ζ . Note that in co-evaporated CuInSe₂-based cells, the defect state ζ , also referred to as N2, is present with high concentration already in the as-grown state, such that it can easily be detected using admittance spectroscopy. In that

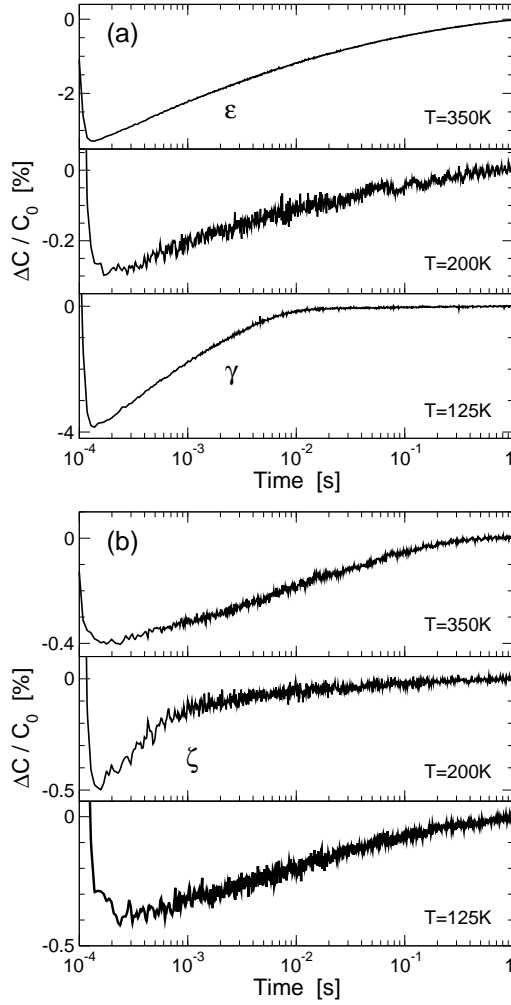


FIG. 2: Capacitance transients of (a) an as-grown and (b) DH-treated (144h) Cu(In,Ga)(S,Se)_2 heterojunction sample at different temperatures. The 1.5V filling pulse of $100\mu\text{s}$ length was superimposed on a quiescent reverse bias of -1.5V.

cell type, its concentration is proportional to the time elapsed under DH conditions¹¹. The defect level ζ is probably intrinsic¹². Taking theoretical considerations into account¹⁰, ζ might be a Cu_{In} antisite.

The temperature-dependent emission rates of the three bulk defect states are displayed in the Arrhenius plot, fig. 3. For the deep trap ϵ , only the majority-carrier response is presented. We are not able to present the quantitative changes of the trap concentrations, as their determination is complicated by several circumstances: First, the transient amplitude strongly depends on temperature, indicating the influence of a temperature-dependent capture cross-section and leakage currents (especially for the DH treated device) on the amplitude¹³. Also, the transient is non-exponential, and both amplitude and decay strongly depend on the width of the filling pulse. The qualitative trap concentrations of the two defect states γ and ϵ decrease due to the DH treatment, whereas the trap level ζ shows a concentration increase.

Our experimental findings can only be seen as a starting

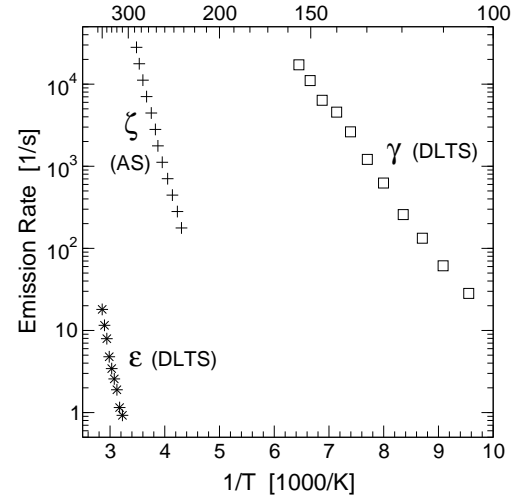


FIG. 3: Arrhenius plot of the three defect states γ (acceptor), ζ (acceptor), and ϵ (recombination center). The abbreviation AS stands for admittance spectroscopy.

point for an identification of the causes of DH induced solar cell degradation. On one hand, further study is needed to gain more insight into the correlation of electronic and chemical modifications. On the other hand, a quantification of the defect state concentrations is crucial for modelling the implications of the DH treatment on the electronic device properties.

To summarize our experimental results, we observed major changes of the Cu(In,Ga)(S,Se)_2 absorber layer and the $\text{CdS/Cu(In,Ga)(S,Se)}_2$ interface due to damp-heat treatment of Cu(In,Ga)(S,Se)_2 -based solar cells and Schottky contacts. We found a reduced band bending and a decreased net doping density in the chalcopyrite absorber layer. Three absorber bulk traps with non-exponential capacitance transients were detected, qualitatively their net concentration decreases due to the damp-heat treatment. The observation of a hysteresis in the current-voltage characteristics of damp-heat treated heterojunctions and Schottky contacts indicates an increased concentration of traps in the absorber layer. The Fermi-level pinning at the buffer/chalcopyrite interface, maintaining a high band bending in as-grown cells, is lifted due to the damp-heat exposure. The combination of these effects represent a major part of the damp-heat induced device degradation.

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